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Laser surface induced roughening of polymeric materials and the effects on Wettability Characteristics

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Abstract

It has been thoroughly demonstrated previously that lasers hold the ability to modulate surface properties of polymers with the result being utilization of such lasers in both research and industry. With increased applications of wettability techniques within industries there is greater need of predicting related characteristics, post laser processing, since such work evaluates the effectiveness of these surface treatments. This paper details the use of a Synrad CO_2 laser marking system to surface roughen polymeric materials, namely: nylon 6,6; nylon 12, polytetrafluoroethylene (PTFE) and polyethylene (PE). These laser-modified surfaces have been analyzed using 3D surface profilometry to ascertain the surface roughness with the wettability characteristics obtained using a wettability goniometer. From the surface roughness results, for each of the samples, generic wettability characteristics arising from laser surface roughening is discussed.

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Keywords: CO_2 laser; surface roughness; wettability characteristics; contact angle; polymers

1. Introduction

When two materials interact, the scientific term “wetting” is a fundamental phenomenon that can be taken into account when predicting how two materials will adhere to one another. The understanding of wetting of a surface by a liquid, leading to the spreading of those liquids over the surface, can be seen as a crucial factor that is adopted within surface chemistry and surface engineering including applications such as biomaterials (Waugh & Lawrence, 2011; Waugh, Lawrence, Morgan, & Thomas, 2009) and coating technologies (Harnett, Alderman, & Wood, 2007; Zhao, Wang, & Liu, 2007). As demonstrated in current surface engineering literature, wettability characteristics of many materials can be altered by the means of laser-induced surface treatment (Khosroshahi, Mahmoodi, Tavakoli, & M., 2008; Liang, Lehr, Danielczak, Leask, & Kietzig, 2014; Waugh & Lawrence, 2011) and other surface treatments (Y. C. Jung & Bhushan, 2006; Y.C. Jung & Bhushan, 2007; Zanini, Barni, Della Pergola, & Riccardi, 2014). Despite increased academic recognition and demand for greater industrial deployment, wetting and the effects of surface modification are still not fully understood within the engineering community. As a result, there is greater need of predicting wettability characteristics post laser processing since such work not only provides evidence for feasibility studies but also quantitatively evaluates the effectiveness of surface treatment.

Laser surface treatment offers numerous advantages such as it can be accurate, precise and non-contact allowing one to see that this can be a relatively clean process. In addition, with small heat affected zones lasers allow one to have the ability to modify both the surface chemistry and topography simultaneously without changing the bulk properties which may already be sufficient for the intended application. Furthermore, lasers also offer the opportunity of inducing varying levels of topography depending on how the laser is employed. For instance, periodic patterns can be induced using a focused beam whereas a more random pattern can be employed using a larger, more divergent, laser beam. Specific to polymers, infra-red lasers give rise to resonant coupling in the form of bond and lattice vibrations allowing for the processing to be thermolytical. This is due to the fact that the photon is only weakly absorbed by the polymer, with the energy that has been absorbed being distributed to vibrational modes (Skordoulis, Makropoulou, & Serafetinides, 1995). This leads to melting and re-solidification of the material as the laser passes over the polymeric sample.

This work provides an overview of the infra-red CO_2 laser surface roughening of nylon 6,6, nylon 12, polytetrafluoroethylene (PTFE) and polyethylene (PE) and how the treatment effects the roughness and wetting contact angle of the samples.

2. Experimental Technique

A CO_2 laser (60 W Firestar-ti; Synrad, Inc., USA) was employed at varying powers to irradiate the surfaces of nylon 6,6, nylon 12, polytetrafluoroethylene (PTFE), polyethylene (PE) which were initially mechanically cut in to samples of 10 mm x 10 mm x 1 mm. The laser was scanned across the surface of the samples using parallel line scans at varying speeds with a constant distance between the scanned lines of 100 μm. The powers, scan speeds and distance between the scanned lines for each sample are detailed in Table 1.

Table 1: Table showing the power, scan speeds and distance between the scanned parallel lines for each sample.

Sample Type	Power (W)	Scan Speed (mms^{-1})	Distance Between Lines (μm)
Nylon 6,6	7	600	100
Nylon 6,6	10	600	100
Nylon 12	10	600	100
Nylon 12	15	600	100
PTFE	7	600	100
PTFE	10	600	100
PE	10	400	100
PE	15	400	100

Following the laser irradiation both the laser roughened and as-received samples were analyzed using white light interferometry (NewView 500; Zygo Corp., USA) and a wettability goniometer (OCA20; DataPhysics Corp., USA). This enabled surface roughness data and the wettability characteristics to be obtained. In terms of wettability characteristics, the contact angle was determined using triply distilled water and the surface free energy was determined using the OWRK technique by implementing triply distilled water and diiodomethane.

3. Results and Discussion

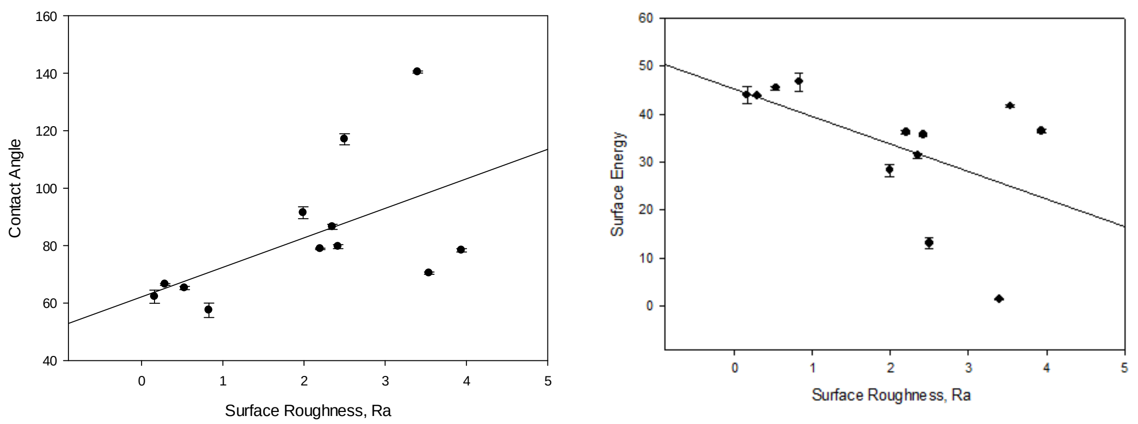
The results for surface roughness, contact angle and surface free energy, for each of the samples, are given in Table 2. As one can see, there were significant variations in the surface roughness when comparing the as-received samples with the corresponding laser surface roughened samples. The nylon 6,6, following laser surface treatment, was rougher with an Ra of 0.83 μm from a laser power of 7 W; whereas a higher power of 10 W gave rise to a smoother surface with an Ra of 0.16 μm. This is likely due to the thermolytical nature of the CO_2 laser-material interaction, bringing about a melting and solidification phenomenon. With regards to the nylon 12 and the PTFE it was observed that the surface roughness increased as a result of the CO_2 laser surface treatment. This is in contrast with the PE which, like the nylon 6,6, gave rise to a surface roughness slightly less than the as-received for 10 W and slightly more than the as-received for 15 W. Again, this is likely due to variations in the melting and solidification phenomenon.

Table 2 also provides the data obtained for the wettability characteristics: the contact angle and the surface free energy. Similar to the surface roughness, the contact angle was significantly modulated as a result of the CO_2 laser roughening. For both the nylon 12 and the PTFE the contact angle increased following laser surface roughening, when compared to the corresponding as-received samples. The contact angle for nylon 6,6 and PE decreased on account of the laser surface roughening and is in contrast with previous work that has been carried out with nylon 6,6 which highlighted a potential mixed state wetting regime resulting in an observed increase in surface roughness (Waugh & Lawrence, 2011; Waugh et al., 2009). This particular result shows that the interface between the liquid and surface is complex and other parameters such as surface chemistry and surface charge need to be accounted for across all of the samples before definite conclusions can be made.

Table 2: Surface roughness and wettability characteristic results for all samples

Sample Type	Power (W)	Scan Speed (mms^{-1})	Surface Roughness, Ra (µm)	Contact Angle (°)	Surface free energy (mJm^{-2})
As-received Nylon 6,6	-	-	0.29	66.49 ± 0.32	43.88 ± 0.20
As-received Nylon 12	-	-	0.53	65.23 ± 0.54	45.43 ±0.33
As-received PTFE	-	-	1.99	91.40 ± 2.05	28.35 ± 1.27
As-received PE	-	-	2.35	86.53 ± 0.90	31.39 ± 0.51
Nylon 6,6	7	600	0.83	57.50 ± 2.50	46.69 ± 1.94
Nylon 6,6	10	600	0.16	62.20 ± 2.30	44.00 ± 1.80
Nylon 12	10	600	3.54	70.40 ± 0.37	41.63 ± 0.23
Nylon 12	15	600	3.94	78.34 ±0.59	36.52 ± 0.37
PTFE	7	600	2.50	117.03 ± 1.93	13.15 ± 1.03
PTFE	10	600	3.40	140.44 ± 0.33	1.48 ± 0.06
PE	10	400	2.20	78.87 ± 0.23	36.19 ± 0.41
PE	15	400	2.42	79.64 ± 0.71	35.71 ± 0.44

In order to identify any trends between the surface roughness and contact angle/surface energy graphs were drawn as shown in Figure 1. Figure 1(a) shows that for all but four samples, there appears to be a linear trend whereby the contact angle increases on account of surface roughness. The four samples with a greater surface roughness of 2.5 µm gave rise to results which do not fit this linear trend. The two samples with Ra values of 2.5 µm and 3.4 µm, giving rise to contact angles of 117° and 140°, respectively, relate to the laser surface roughened PTFE. The other two samples with Ra values of 3.54 µm and 3.94 µm, giving rise to contact angles of 70° and 78°, respectively, relate to the laser surface roughened nylon 12. These results have a considerable impact upon the location of the trend line. For instance, if one was to neglect the nylon 12 or PTFE laser surface roughened results the gradient of the trend line would be significantly increased or decreased, respectively. As would be expected, the inverse of the trend line is seen in Figure 1(b) when accounting for the surface energy with respect to the surface roughness.



(a) (b)

Figure 1: (a) Graph showing surface roughness, Ra (µm) against contact angle, θ (°) for all samples and (b) Graph showing surface roughness, Ra (µm) against surface energy (mJm^{-2}) for all samples.

The material variations from polymer to polymer is believed to be one of the main reasons as to the modulation in laser-material interaction and resulting wettability characteristics. For instance, the major differences between nylon 6,6 and nylon 12 are that nylon 6,6 has higher strength, stiffness and temperature resistance than nylon 12, but it does have higher water absorption and less chemical resistance. These properties are the result of the polymer chain structure as the nylon 6,6 has more amide linkages per chain meaning that it has more inter-chain bonding. As these differences in material properties along with their differing optical properties will likely have an effect on the laser-material interaction further research is required. As such, with further work, it may be seen that the nylon 12, under CO_2 laser treatment, produces a different surface functionality when compared to nylon 6,6, PTFE and PE. For instance, more OH functionalization may develop giving rise to an increased wettability, as discussed by Zanini *et al.* (Zanini et al., 2014). This could possibly be the reason why a reduction of the contact angle has been observed for the nylon 12 even when the laser surface roughened nylon 12 produces the largest roughness values of over 3.5 μm. Furthermore, as PTFE is a fluorocarbon, meaning that it only contains fluorine and carbon, the emergence of oxygen containing functional groups, arising from the melting and re-solidification process of the laser surface roughening, could have had a large impact upon the contact angle, enabling the PTFE to become more hydrophobic. With this in mind, it is important that further work be carried out relating to bond and functionalization analysis of the laser roughened samples so that these hypotheses can be confirmed.

It has been seen that through laser surface roughening the surfaces of a number of polymeric materials can be modified with respect to their wetting and adhesive properties. What is more, it appears from the data that there is a generic trend which could be exploited to predict the wetting nature of laser surface roughened polymeric materials. Only through extended research, however, can these generic trends be verified and tested to ensure that a generic theory of the wetting nature of laser surface treated polymers can be established.

4. Conclusions

This work has successfully shown that CO_2 laser surface roughening has the ability to modify the wettability characteristics and adhesion characteristics of a number of polymeric materials; namely: nylon 6,6, nylon 12, PTFE and PE. What is more, a trend has arisen for many of the samples showing that an increase in surface roughness gave rise to a linear increase in the contact angle. Having said that, it was also apparent that two samples (nylon 12 and PTFE) did not correspond fully to this linear trend. It has been hypothesized within this work that the possibility of surface functionalization has given rise to these two polymeric materials not corresponding to the trend. This; however, requires considerable future work to ascertain whether this is the case. In addition, further work on the effects of other surface parameters, such as surface charge, on the wettability characteristics needs to be conducted to ensure that a comprehensive understanding can be achieved.

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